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Dynamics of a paradigmatic linear polymer: A proton field-cycling NMR relaxometry study on poly(ethylene-propylene)

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Abstract

© 2016 American Chemical Society.The dynamics of melts of linear poly(ethylene-alt-propylene) (PEP) of different molar masses (M) is investigated by 1H field-cycling (FC) NMR relaxometry. Employing a commercial and a home-built relaxometer the spin-lattice relaxation rate R1(ω) is measured in the frequency range of 200 Hz to 30 MHz and the temperature range of 200-400 K. Transforming the FC NMR relaxation data to the susceptibility representation and applying frequency-temperature superposition, master curves for the dipolar correlation function CDD(t/τα) (containing intra- and intermolecular contributions) are constructed which extend up to six decades in amplitude and eight in time. Here, τα is the time scale of the structural (α-) relaxation, which is obtained over several decades. Comparison with previously reported FC data for polybutadiene (PB) discloses very similar CDD(t). Depending on M, all the five relaxation regimes of a polymer melt are covered: in addition to the α-process (0) and the terminal relaxation (IV), which are immanent to all liquids, three polymer-specific power-law regimes (Rouse, I; constraint Rouse, II; and reptation, III) are found, i.e. CDD(t) ∝ t-ϵ. The corresponding exponents (ϵI-III) are close to those predicted by the tube-reptation (TR) model for the segmental translation. In contrast to previous interpretation the intermolecular relaxation dominates CDD(t), in particular in regime II and beyond. The decomposition into intra- (mediated by segmental reorientation) and intermolecular relaxation (mediated by segmental translation) via isotope dilution experiments yields Cinter(t) = Ctrans(t) ∝ t-0.28±0.05 concerning PEP and Cinter(t) ∝ t-0.30±0.05 concerning PB for regime II (high-M limit). For the reorientational correlation function Cintra(t) = C2(t) ∝ t-0.50±0.05 (PEP) and C2(t) ∝ t-0.45±0.05 (PB) are obtained. These exponents ϵIIintra are at variance with ϵIITR = 0.25 predicted by the TR model. The fact that translation conforms to the TR model, while reorientation does not, now confirmed for the two polymers PEP and PB, challenges de Gennes' return-to-origin hypothesis which assumes strong translational-rotational coupling in the TR model.

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